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(54) **METHODE DE PREPARATION DE POLYMERES D'ETHYLENE**  
(54) **PROCESS FOR THE PREPARATION OF ETHYLENE  
POLYMERS**

(57) The preparation of polyethylene and ethylene-1-olefin copolymers in the suspension or gas phase process with the aid of metallocene/aluminoxane catalysts whose metallocene component is a bridged biscyclopentadienyl complex offers particular advantages. Depending on the structure of the complex, the use of these complexes gives, with high activity, products in a very broad molecular-weight range and permits the production of very varied grain morphologies of the products, such as high and low bulk density, extremely small and extremely large mean grain diameters and various grain shapes. The variety of grain morphologies which can be achieved opens up various possibilities for the use of such polyethylene powders in sintering processes.

**ABSTRACT OF THE DISCLOSURE****Process for the preparation of ethylene polymers**

The preparation of polyethylene and ethylene-1-olefin copolymers in the suspension or gas phase process with the aid of metallocene/aluminoxane catalysts whose metallocene component is a bridged biscyclopentadienyl complex offers particular advantages.

Depending on the structure of the complex, the use of these complexes gives, with high activity, products in a very broad molecular-weight range and permits the production of very varied grain morphologies of the products, such as high and low bulk density, extremely small and extremely large mean grain diameters and various grain shapes. The variety of grain morphologies which can be achieved opens up various possibilities for the use of such polyethylene powders in sintering processes.

## Description

## Process for the preparation of ethylene polymers

5 The present invention relates to a process for the preparation of polyethylene and ethylene-1-olefin copolymers of various molecular weight ranges with the aid of metallocene/aluminoxane catalysts.

10 A process for the preparation of polyethylene with the aid of metallocene/aluminoxane catalysts in toluene as suspending agent has already been described [cf. EP 69,951]. The molecular weights achieved for the polymers are relatively low. No data is given on the morphology of the polymers.

15 Furthermore, a comparable process using a high-boiling hydrocarbon as suspending agent has been disclosed (cf. EP 170,059). However, the catalyst activities are moderate, and the bulk densities achieved for the polymer are between 0.15 and 0.18 g/cm<sup>3</sup>.

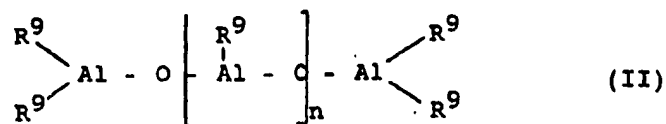
20 Furthermore, processes have been described for the preparation of polyethylene and ethylene-1-olefin copolymers with the aid of metallocene/aluminoxane catalysts by polymerization in the gas phase (cf. EP 206,794, 285,443 and 294,942). Here too, only moderately high molecular weights of the polymers and in most cases only poor  
25 activities of the catalysts are achieved.

30 It is common to all the abovementioned processes that, as the metallocene, unbridged biscyclopentadienylzirconium complexes are employed in which the cyclopentadienyl radicals are substituted or unsubstituted, and the metallocene is either employed as such in the polymerization or has been linked to an inert support by appropriate preliminary reaction steps.

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It has now been found that the preparation of polyethylene and ethylene-1-olefin copolymers by suspension or gas-phase processes with the aid of metallocene/aluminoxane catalysts whose metallocene component is a bridged  
 5 biscyclopentadienyl complex offers important advantages.

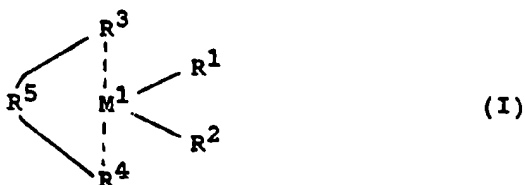
The invention thus relates to a process for the preparation of ethylene polymers by polymerization of ethylene or copolymerization of ethylene with 1-olefins having 3 to 20 carbon atoms at a temperature of from -60 to 200°C  
 10 and a pressure of from 0.5 to 200 bar in solution, in suspension or in the gas phase, in the presence of a catalyst comprising a metallocene as the transition-metal component and an aluminoxane of the formula II



15 for the linear type and/or of the formula III



for the cyclic type, where, in the formulae II and III, R<sup>9</sup> is a C<sub>1</sub>-C<sub>6</sub>-alkyl group or phenyl or benzyl, and n is an integer from 2 to 50, which comprises carrying out the  
 20 polymerization in the presence of a catalyst whose transition-metal component is a compound of the formula I



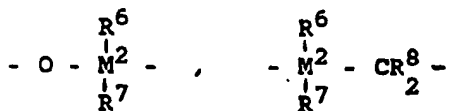
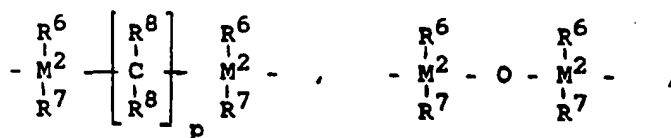
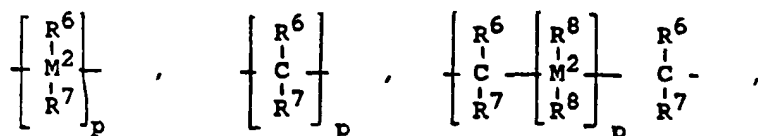
in which

25 M<sup>1</sup> is titanium, zirconium, hafnium, vanadium, niobium or tantalum,  
 R<sup>1</sup> and R<sup>2</sup> are identical or different and are a hydrogen

atom, a halogen atom, a C<sub>1</sub>-C<sub>10</sub>-alkyl group, a C<sub>1</sub>-C<sub>10</sub>-alkoxy group, a C<sub>6</sub>-C<sub>10</sub>-aryl group, a C<sub>6</sub>-C<sub>10</sub>-aryloxy group, a C<sub>2</sub>-C<sub>10</sub>-alkenyl group, a C<sub>7</sub>-C<sub>40</sub>-arylalkyl group, a C<sub>7</sub>-C<sub>40</sub>-alkylaryl group or a C<sub>6</sub>-C<sub>40</sub>-arylalkenyl group,

R<sup>3</sup> and R<sup>4</sup> are identical or different and are a mono-nuclear or polynuclear hydrocarbon radical which, with the central atom M<sup>1</sup>, is able to form a sandwich structure,

10 R<sup>5</sup> is

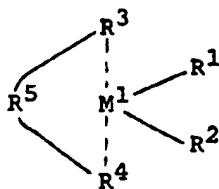


=BR<sup>6</sup>, =AlR<sup>6</sup>, -Ge-, -Sn-, -O-, -S-, =SO, =SO<sub>2</sub>, =NR<sup>6</sup>, =CO, =PR<sup>6</sup> or =P(O)R<sup>6</sup>, where R<sup>6</sup>, R<sup>7</sup> and R<sup>8</sup> are identical or different and are a hydrogen atom, a halogen atom, a C<sub>1</sub>-C<sub>10</sub>-alkyl group, a C<sub>1</sub>-C<sub>10</sub>-fluoroalkyl group, a C<sub>6</sub>-C<sub>10</sub>-fluoroaryl group, a C<sub>6</sub>-C<sub>10</sub>-aryl group, a C<sub>1</sub>-C<sub>10</sub>-alkoxy group, a C<sub>2</sub>-C<sub>10</sub>-alkenyl group, a C<sub>7</sub>-C<sub>40</sub>-arylalkyl group, a C<sub>6</sub>-C<sub>40</sub>-arylalkenyl group or a C<sub>7</sub>-C<sub>40</sub>-alkylaryl group, or R<sup>6</sup> and R<sup>7</sup> or R<sup>6</sup> and R<sup>8</sup>, in each case with the atoms connecting them, form a ring,

M<sup>2</sup> is silicon, germanium or tin, and

p is the number 1, 2, 3, 4 or 5.

25 The catalyst to be used for the process according to the invention comprises an aluminoxane and a metallocene of the formula I



(I).

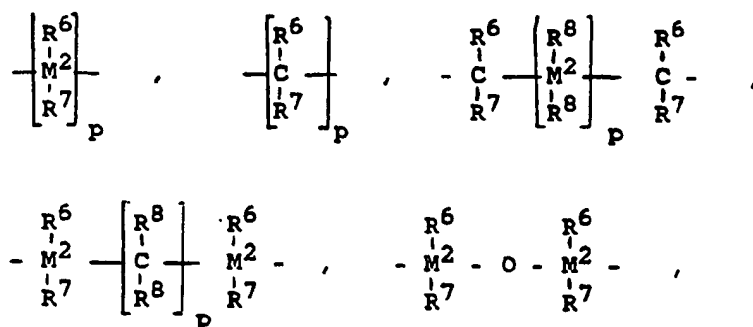
In the formula I,  $M^1$  is a metal selected from the group comprising titanium, zirconium, hafnium, vanadium, niobium and tantalum, preferably zirconium.

- 5  $R^1$  and  $R^2$  are identical or different and are a hydrogen atom, a  $C_1-C_{10}$ -, preferably  $C_1-C_3$ -alkyl group, a  $C_1-C_{10}$ -, preferably  $C_1-C_3$ -alkoxy group, a  $C_6-C_{10}$ -, preferably  $C_6-C_8$ -aryl group, a  $C_6-C_{10}$ -, preferably  $C_6-C_8$ -aryloxy group, a  $C_2-C_{10}$ -, preferably  $C_2-C_4$ -alkenyl group, a  $C_7-C_{40}$ -, preferably  $C_7-C_{10}$ -arylalkyl group, a  $C_7-C_{40}$ -, preferably  $C_7-C_{12}$ -alkylaryl group, a  $C_8-C_{40}$ -, preferably  $C_8-C_{12}$ -arylalkenyl group or a halogen atom, preferably chlorine.
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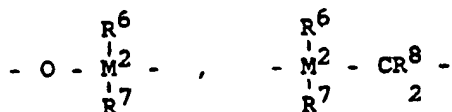
- 15  $R^3$  and  $R^4$  are identical or different and are a mononuclear or polynuclear hydrocarbon radical which, together with the central atom  $M^1$ , is able to form a sandwich structure.

$R^3$  and  $R^4$  are preferably cyclopentadienyl, indenyl, tetrahydroindenyl or fluorenyl, it also being possible for the basic structures to carry additional substituents.

- 20  $R^5$  is a mono- or polymembered bridge which links the radicals  $R^3$  and  $R^4$  and is



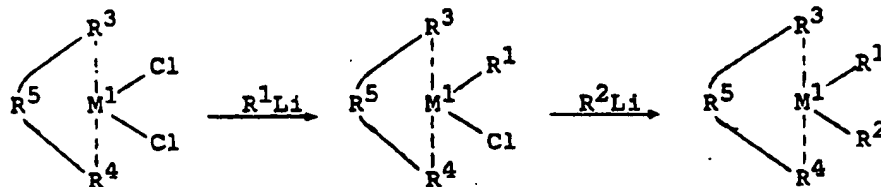
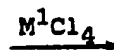
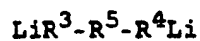
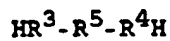
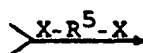
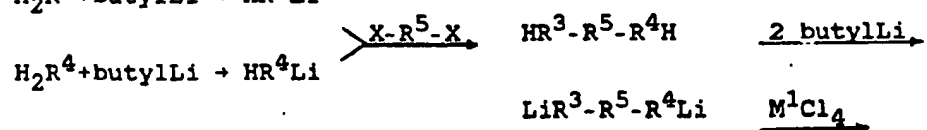
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- 5  $=BR^6$ ,  $=AlR^6$ ,  $-Ge-$ ,  $-Sn-$ ,  $-O-$ ,  $-S-$ ,  $=SO$ ,  $=SO_2$ ,  $=NR^6$ ,  
 $=CO$ ,  $=PR^6$  or  $=P(O)R^6$ , where  $R^6$ ,  $R^7$  and  $R^8$  are identi-  
 cal or different and are a hydrogen atom, a halogen  
 atom, preferably chlorine, a  $C_1-C_{10}-$ , preferably  $C_1-$   
 $C_3-$ alkyl group, in particular a methyl group, a  $C_1-$   
 $C_{10}$ -fluoroalkyl group, preferably a  $CF_3$  group, a  $C_6-$   
 $C_{10}$ -fluoroaryl group, preferably a pentafluorophenyl  
 group, a  $C_6-C_{10}-$ , preferably  $C_6-C_8$ -aryl group, a  $C_1-$   
 $C_{10}-$ , preferably  $C_1-C_4$ -alkoxy group, in particular a  
 10 methoxy group, a  $C_2-C_{10}-$ , preferably  $C_2-C_4$ -alkenyl  
 group, a  $C_7-C_{40}-$ , preferably  $C_7-C_{10}$ -arylalkyl group,  
 a  $C_8-C_{40}-$ , preferably  $C_8-C_{12}$ -arylalkenyl group or a  $C_7-$   
 $C_{40}-$ , preferably  $C_7-C_{12}$ -alkylaryl group, or  $R^6$  and  $R^7$   
 or  $R^6$  and  $R^8$  in each case, together with the  
 15 atoms connecting them, form a ring,  
 $M^2$  is silicon, germanium or tin, preferably silicon or  
 germanium, and  
 $p$  is the number 1, 2, 3, 4 or 5.

- Particularly preferred metallocenes are:  
 20  $rac$ -dimethylsilylbis(1-indenyl)zirconium dichloride,  
 $rac$ -diphenylsilylbis(1-indenyl)zirconium dichloride,  
 1-silacyclobutylbis(1'-indenyl)zirconium dichloride,  
 $rac$ -dimethylsilylbis(1-(3-methylindenyl))zirconium  
 dichloride,  
 25  $rac$ -1,1,2,2-tetramethyldisilaethylenebis(1'-indenyl)zir-  
 conium dichloride,  
 dimethylsilylbis(1-(3-trimethylsilyl)cyclopentadienyl)-  
 zirconium dichloride, and  
 diphenylmethylen(9-fluorenyl)cyclopentadienylzirconium  
 30 dichloride.

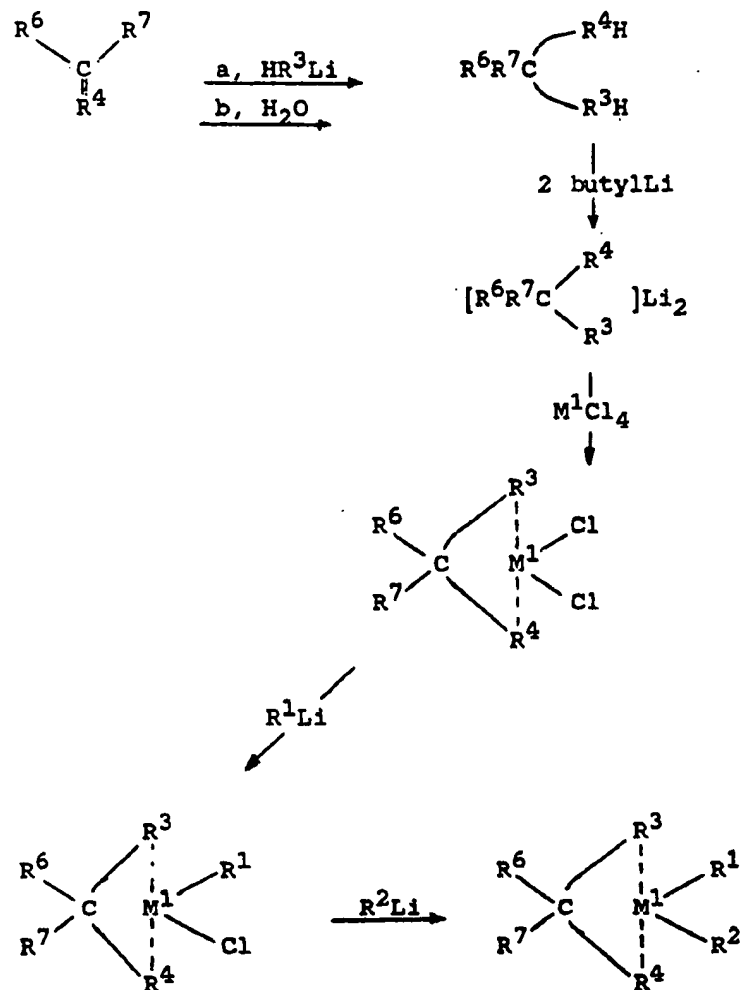
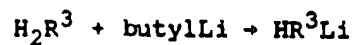
The above-described metallocenes can be prepared by the  
 general reaction scheme below:



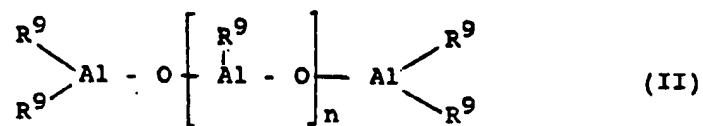
(X = Cl, Br, I, O-tosyl)



or



The cocatalyst is an aluminoxane of the formula II



for the linear type and/or of the formula III



for the cyclic type. In these formulae,  $R^9$  is a  $C_1$ - $C_8$ -alkyl group, preferably methyl, ethyl or isobutyl, butyl or neopentyl, or phenyl or benzyl. Methyl is particularly preferred.  $n$  is an integer from 2 to 50, preferably 5 to 40. However, the exact structure of the aluminoxane is not known.

The aluminoxane can be prepared in various ways.

One possibility is the careful addition of water to a dilute solution of a trialkylaluminum by introducing the solution of the trialkylaluminum, preferably trimethylaluminum, and the water in each case in small portions into an initially introduced larger amount of an inert solvent and between each portion awaiting the end of the evolution of gas.

In another process, finely powdered copper sulfate pentahydrate is slurried in toluene, and, in a glass flask under an inert gas at about  $-20^\circ C$ , sufficient trialkylaluminum is added so that about 1 mole of  $CuSO_4 \cdot 5H_2O$  is available for each 4 Al atoms. After slow hydrolysis with elimination of alkane, the reaction mixture is left at room temperature for 24 to 48 hours, cooling possibly being needed to ensure that the temperature does not exceed  $30^\circ C$ . The aluminoxane dissolved in the toluene is subsequently filtered off from the copper sulfate, and the solution is evaporated in vacuo. It is assumed that the low-molecular-weight aluminoxanes condense in these preparation processes to form higher oligomers with elimination of trialkylaluminum.

Furthermore, aluminoxanes are obtained if trialkylaluminum, preferably trimethylaluminum, dissolved in an inert aliphatic or aromatic solvent, preferably heptane or

toluene, is reacted at a temperatur of from -20 to 100°C with aluminum salts, preferably aluminum sulfate, containing water of crystallization. In this case, the volume rati betwe n the solvent and the alkylaluminum  
5 used is 1:1 to 50:1 - preferably 5:1 - and the reaction time, which can be monitored from the elimination of the alkane, is 1 to 200 hours - preferably 10 to 40 hours.

Of the aluminum salts containing water of crystalliza-  
tion, those are particularly used which have a high  
10 content of water of crystallization. Aluminum sulfate hydrate, in particular the compounds  $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$  and  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  having the particularly high water of crystallization content of 16 and 18 moles of  $\text{H}_2\text{O}$ /mole of  $\text{Al}_2(\text{SO}_4)_3$ , respectively, is particularly preferred.

15 A further variant for the preparation of aluminoxane is to dissolve trialkylaluminum, preferably trimethylaluminum, in the suspending agent initially introduced into the polymerization reactor and then to react the aluminum compound with water.

20 Besides the above-outlined processes for the preparation of aluminoxanes, there are others which can be used.

Irrespective of the manner of preparation, all alumin-  
oxane solutions have in common a varying content of  
unreacted trialkylaluminum, which is in free form or in  
25 the form of an adduct. This content has an effect, as yet not explained accurately, on the catalytic effectiveness, which varies depending on the metallocene compound employed.

30 It is possible to pre-activate the metallocene using an aluminoxane of the formula II and/or III before using the polymerization reaction. This considerably increases the polymerization activity and improves the grain morphology.

5 The preactivation of the transition-metal compound is carried out in solution. It is preferred here to dissolve the metallocene in a solution of the aluminoxane in an inert hydrocarbon. Suitable inert hydrocarbons are aliphatic or aromatic hydrocarbons. Toluene is preferably used.

10 The concentration of the aluminoxane in the solution is in the range from about 1% by weight to the saturation limit, preferably from 5 to 30% by weight, in each case relative to the total solution. The metallocene can be employed in the same concentration, but it is preferably employed in an amount of from  $10^{-4}$  - 1 mole per mole of aluminoxane. The pre-activation time is 5 minutes to 60 hours, preferably 5 to 60 minutes. The pre-activation is carried out at a temperature of from  $-78^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ , preferably 0 to  $70^{\circ}\text{C}$ .

20 A significantly longer preactivation is possible, but normally has neither an activity-increasing nor activity-reducing effect, but may be entirely appropriate for storage purposes.

25 The polymerization is carried out in a known manner in solution, in suspension or in the gas phase, continuously or batchwise, in one or more steps, at a temperature of from  $-60$  to  $200^{\circ}\text{C}$ , preferably  $-30$  to  $120^{\circ}\text{C}$ , in particular 50 to  $90^{\circ}\text{C}$ .

30 The overall pressure in the polymerization system is 0.5 to 200 bar. The polymerization is preferably carried out in the industrially particularly interesting pressure range of from 5 to 60 bar. The metallocene compound is used here in a concentration, relative to the transition metal, of from  $10^{-3}$  to  $10^{-8}$ , preferably  $10^{-4}$  to  $10^{-7}$  mole of transition metal per  $\text{dm}^3$  of solvent or per  $\text{dm}^3$  of reactor volume. The aluminoxane is used in a concentration of from  $10^{-5}$  to  $10^{-1}$  mole, preferably  $10^{-3}$  to  $10^{-2}$  mole per  $\text{dm}^3$  of solvent or per  $\text{dm}^3$  of reactor volume. In

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principle, however, higher concentrations are also possible.

5 If the polymerization is carried out as a suspension or solution polymerization, a solvent which is inert towards Ziegler catalysts is used, i.e. an aliphatic or aromatic hydrocarbon. Aliphatic hydrocarbons are preferred, such as, for example, butane, pentane, hexane, heptane, isooctane, cyclohexane, methylcyclohexane or petroleum or hydrogenated diesel oil fractions.

10 Besides homopolymerization of ethylene, the catalyst systems according to the invention are employed for the copolymerization of ethylene with a 1-olefin having 3 to 20 carbon atoms. Examples of such 1-olefins are propylene, 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene.

15 The molecular weight of the polymer can be regulated in a known manner, preferably using hydrogen.

The polymerization can have any desired duration, since the catalyst system to be used according to the invention only exhibits a slight time-dependent decrease in polymerization activity.

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Depending on the structure of the complex, the use of these complexes gives, with high activities, polyethylene and ethylene-1-olefin copolymers having a narrow molecular-weight distribution (polydispersity) in a broad molecular-weight range, in particular products having high molecular weights which are suitable for processing by injection molding and extrusion and in particular have high stretching capacity of the polymer melt, and permits the production of very varied grain morphologies of the product, such as high and low bulk densities, extremely small and extremely large mean grain diameters and various grain shapes. The variety of grain morphologies which can be achieved opens up various possibilities for the use of such polyethylene powders in sintering processes.

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The examples below are intended to illustrate the invention.

The abbreviations have the following meanings:

- 5 VN = viscosity number in  $\text{cm}^3/\text{g}$ ,
- $M_w$  = weight average molecular weight in  $\text{g/mol}$ ,
- $M_w/M_n$  = molecular weight distribution determined by gel permeation chromatography (GPC),
- $d_{50}$  = mean grain diameter in  $\mu\text{m}$ .

10 The pressure data in the examples are in bar of super-atmospheric pressure.

The densities of the copolymers have been determined in accordance with DIN 53479, method A.

All the operations below were carried out under a protective gas using absolute solvents.

15 **Example 1:**

**Preparation of dimethylsilylbis(1-indenyl)**

80  $\text{cm}^3$  (0.20 mol) of a 2.5 molar solution of n-butyllithium in hexane were added with ice cooling to a solution of 30 g (0.23 mol) of indene (technical grade, ~91%) which has been filtered through aluminum oxide. The batch was stirred for a further 15 minutes at room temperature, and the orange solution was added via a hollow needle over the course of 2 hours to a solution of 13.0 g (0.10 mol) of dimethyldichlorosilane (99%) in 30  $\text{cm}^3$  of diethyl ether. The orange suspension was stirred overnight and washed by shaking three times with 100-150  $\text{cm}^3$  of water. The yellow organic phase was dried twice over sodium sulfate and evaporated in the reaction evaporator. The orange oil which remained was kept at 40°C for 4 to 5 hours in an oil-pump vacuum and freed from excess indene, during which a white precipitate deposited. Addition of 40  $\text{cm}^3$  of methanol and crystallization at -35°C gave a total of 20.4 g (71%) of the compound

dimethylsilylbis(1-indenyl) as a white to beige powder (2 diastereomers). M.p. 79-81°C.

**Example 2:**

Preparation of rac-dimethylsilylbis(1-indenyl)zirconium dichloride (metallocene A)

5 15.5 cm<sup>3</sup> (38.7 mmol) of a 2.5 molar hexane solution of butyllithium were added slowly at room temperature to a solution of 5.6 g (19.4 mmol) of dimethylsilylbis(1-indenyl) in 40 cm<sup>3</sup> of THF. 1 hour after completion of the

10 addition, the deep red solution was added dropwise over the course of 4-6 hours to a suspension of 7.3 g (19.4 mmol) of ZrCl<sub>4</sub>·2THF in 60 cm<sup>3</sup> of THF. After the mixture had been stirred for 2 hours, the orange precipitate was filtered off with suction via a glass frit and

15 recrystallized from CH<sub>2</sub>Cl<sub>2</sub>, to give 1.0 g (11%) of the metallocene A in the form of orange crystals, which gradually decompose from 200°C.

Correct elementary analyses. The EI mass spectrum exhibited M<sup>+</sup> = 448. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>): 7.04-7.60 (m, 8, arom. H), 6.90 (dd, 2, β-Ind H), 6.08 (d, 2, α-Ind H), 1.12 (s, 6, SiCH<sub>3</sub>).

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**Example 3:**

Preparation of rac-diphenylsilylbis(1-indenyl)zirconium dichloride (metallocene B)

25 A solution of 20 g (48.5 mmol) of (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si(Ind)<sub>2</sub>, prepared from (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SiCl<sub>2</sub> and indenyllithium analogously to Example 1, in 200 cm<sup>3</sup> of diethyl ether was reacted at 0°C with 40 cm<sup>3</sup> (100 mmol) of butyllithium (2.5 molar in hexane). After the mixture had been stirred at room temperature

30 for 2 hours, the solvent was stripped off, and the residue was stirred with 100 cm<sup>3</sup> of hexane and filtered off. The dilithio salt was dried in an oil-pump vacuum and added to a suspension of 11.3 g (48.5 mmol) of ZrCl<sub>4</sub> in 150 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub> at -78°C. The mixture was stirred

overnight and allowed to warm to room temperature. The red solution was concentrated, and the precipitate which deposited was filtered off via a frit. Extraction with toluene gave 2.0 g (7%) of metallocene B as an orange powder. Correct elementary analyses.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ): 6.8-8.2 (m, 18, arom. H), 7.03 (dd, 2,  $\beta$ -Ind H), 6.30 (d, 2,  $\alpha$ -Ind H).

Example 4:

Preparation of rac-dimethylsilylbis(1-(3-methylindenyl))-zirconium dichloride (metallocene G)  
A solution of 4.89 g (15.5 mmol) of  $(\text{CH}_3)_2\text{Si}(\text{MeInd})_2$ , prepared analogously to Example 1 from  $(\text{CH}_3)_2\text{SiCl}_2$  and 3-methylindenyllithium, was reacted with 12.5  $\text{cm}^3$  (30.5 mmol) of butyllithium and 5.84 g (15.5 mmol) of  $\text{ZrCl}_4 \cdot 2\text{THF}$  analogously to Example 2. After the solvent had been stripped off, the residue was extracted with toluene. The precipitate which deposited from toluene on concentration and cooling was recrystallized from  $\text{CHCl}_3$ , to give 800 mg (10%) of metallocene G in the form of orange-red crystals. Correct elementary analyses.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ): 7.0-7.5 (m, 8, arom. H), 5.71 (s, 2,  $\alpha$ -Ind H), 2.30 (s, 6, Ind  $\text{CH}_3$ ), 1.07 (s, 6,  $\text{SiCH}_3$ ).

Example 5:

Preparation of dimethylsilylbis(1-(3-trimethylsilyl)-cyclopentadienyl)zirconium dichloride (metallocene K)  
A solution of 3.9 g (11.7 mmol) of  $(\text{CH}_3)_2\text{Si}[(\text{CH}_3)_3\text{SiCp}]_2$ , prepared from  $\text{Li}_2[(\text{CH}_3)_2\text{Si}(\text{Cp})_2]$  and  $(\text{CH}_3)_3\text{SiCl}$ , was reacted analogously to Example 2 with 9.4  $\text{cm}^3$  (23.4 mmol) of butyllithium and 4.4 g (11.7 mmol) of  $\text{ZrCl}_4 \cdot 2\text{THF}$ . After the solvent had been stripped off, the residue was extracted with diethyl ether. The residue remaining after the diethyl ether had been stripped off was recrystallized from  $\text{CHCl}_3$ , to give 0.8 g (14%) of the complex as beige crystals. Correct elementary analyses.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ): 6.95 (dd, 2, CpH), 6.12 (t, 2, CpH), 5.96 (t, 2,



CpH), 0.72 (s, 6, Si(CH<sub>3</sub>)<sub>2</sub>), 0.25 (s, 9, Si(CH<sub>3</sub>)<sub>3</sub>). The NMR spectrum showed that metallocene K was in the form of an isomer mixture (43% of the rac-isomer, 57% of the meso-isomer).

5 Example 6:

Preparation of isopropyl(1-indenyl)cyclopentadienylzirconium dichloride (metallocene P)

19 cm<sup>3</sup> (47.3 mmol) of butyllithium (2.5 molar in hexane) were added at room temperature to a solution of 6.0 g (47 mmol) of indene (91%) in 100 cm<sup>3</sup> of diethyl ether. After 1 hour, this solution was added to a solution of 6,6-dimethylfulvene in 100 cm<sup>3</sup> of diethyl ether at -78°C. After the mixture had been stirred at room temperature for 16 hours, the orange solution was diluted with 400 cm<sup>3</sup> of diethyl ether, and 100 cm<sup>3</sup> of water were added. The yellow organic phase was then washed twice with water, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The brown oil remaining was chromatographed on 400 g of silica gel 60. Using hexane + 7% of methylene chloride, a total of 7.2 g (68%) of the compound isopropyl(1-indenyl)cyclopentadienyl were eluted as a yellow oil (2 isomers). 28 cm<sup>3</sup> (70 mmol) of butyllithium (2.5 molar in hexane) were added at 0°C to a solution of 7.1 g (32 mmol) of this compound in 100 cm<sup>3</sup> of diethyl ether. After the mixture had been stirred at room temperature for 2 hours, the yellow precipitate was filtered off via a glass frit and washed with hexane/diethyl ether (1:1). After the precipitate had been dried in an oil-pump vacuum the pale yellow powder was added at -78°C to a suspension of 7.5 g (32 mmol) of ZrCl<sub>4</sub> in 100 cm<sup>3</sup> of methylene chloride. The mixture was slowly warmed to room temperature, stirred at room temperature for 30 minutes and filtered via a glass frit, and the solid was washed several times with methylene chloride. The yellow filtrate was concentrated until crystallization occurred. At -35°C, a total of 2.4 g (19%) of the complex rac-[(CH<sub>3</sub>)<sub>2</sub>C(Ind)Cp]ZrCl<sub>2</sub> crystallized in the form of yellow-orange crystals. Correct elementary analyses.

<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>): 6.90-7.75 (m, 4, arom. H), 6.85 (dd, 1, β-Ind-H), 6.52 (m, 2, Cp-H), 6.12 (d, 1, α-Ind-H), 5.82, 5.70 (2 x q, 2 x 1, Cp-H), 2.20; 1.95 (2 x s, 2 x 3, CH<sub>3</sub>).

5      **Example 7:**

**Preparation of diphenylmethylen(9-fluorenyl)cyclopentadienylzirconium dichloride (metallocene Q)**

12.3 cm<sup>3</sup> (30.7 mmol) of a 2.5 molar hexane solution of n-butyllithium were slowly added at room temperature to  
10 a solution of 5.10 g (30.7 mmol) of fluorene in 60 cm<sup>3</sup> of THF. After 40 minutes, 7.07 g (30.7 mmol) of diphenylfulvene were added to the orange solution, and the mixture was stirred overnight. 60 cm<sup>3</sup> of water were added to the dark red solution, whereupon the solution became yellow,  
15 and the solution was extracted using ether. The ether phase, dried over MgSO<sub>4</sub>, was concentrated and left to crystallize at -35°C, to give 5.1 g (42%) of 1,1-cyclopentadienyl(9-fluorenyl)diphenylmethane as a beige powder.

2.0 g (5.0 mmol) of the compound were dissolved in 20 cm<sup>3</sup> of THF, and 6.4 cm<sup>3</sup> (10 mmol) of a 1.6 molar solution of butyllithium in hexane were added at 0°C. After the mixture had been stirred at room temperature for 15 minutes, the solvent was stripped off, and the red residue was  
25 dried in an oil-pump vacuum and washed several times with hexane. After the residue had been dried in an oil-pump vacuum, the red powder was added at -78°C to a suspension of 1.16 g (5.0 mmol) of ZrCl<sub>4</sub>. The batch was slowly warmed and stirred for a further 2 hours at room temperature.  
30 The pink suspension was filtered via a G3 frit. The pink residue was washed with 20 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub>, dried in an oil-pump vacuum and extracted with 120 cm<sup>3</sup> of toluene. Stripping off of the solvent and drying in an oil-pump vacuum gave 0.55 g of the zirconium complex (metallocene Q) in  
35 the form of a pink crystal powder.

The orange-red filtrate of the reaction batch was evaporated and left to crystallize at  $-35^{\circ}\text{C}$ . A further 0.34 g of the complex crystallizes from  $\text{CH}_2\text{Cl}_2$ . Total yield 1.0 g (36%). Correct elementary analyses. The mass spectrum exhibited  $M^+ = 556$ .  $^1\text{H}$  NMR spectrum (100 MHz,  $\text{CDCl}_3$ ): 6.90-8.25 (m, 16, Flu-H, Ph-H), 6.40 (m, 2, Ph-H), 6.37 (t, 2, Cp-H), 5.80 (t, 2, Cp-H).

#### Examples 8-18:

The metallocenes C, D, E, F, H, I, L, M, N, O and R of Table 2 were prepared analogously to Examples 1 and 2. The dimethylchlorosilane in Example 1 was replaced here by appropriate other dihalogen compounds, which are shown in Table 1. In the case of complexes substituted on the 5-membered ring (metallocenes N and O), an indene correspondingly substituted on the 5-membered ring was employed (analogously to Example 4). In the case of the hafnium complex metallocene R,  $\text{ZrCl}_4$  in Example 2 was replaced by  $\text{HfCl}_4$ .

Table 1

Example	Metallocene	Dihalogen compound
8	C	phenylmethyldichlorosilane
9	D	phenylvinylchlorosilane
10	E	dimethyldichlorogermanium
11	F	cyclotrimethylenedichlorosilane
12	H	1,1,2,2-tetramethyl-1,2-dichlorodisilane
13	I	1,2-bis(chlorodimethylsilyl)-ethane
14	L	1,2-dibromoethane
15	M	1,3-dibromopropane
16	N	1,2-dibromoethane
17	O	1,2-dibromoethane
18	R	1,1,2,2-tetramethyl-1,2-dichlorosilane

**Example 19:**

**Preparation of phenylmethylethylene(9-fluorenyl)cyclopentadienylniobium dichloride (metallocene T)**

The metallocene T was prepared analogously to Example 7. However, the diphenylfulvene and  $ZrCl_4$  in Example 7 were replaced by phenylmethylethylene and  $HfCl_4$ .

**Example 20:**

10 dm<sup>3</sup> of a petroleum ether (boiling range 100-120°C) were introduced at 20°C into a dry 16 dm<sup>3</sup> reactor which had been flushed with nitrogen. The gas space of the reactor was then flushed free from nitrogen by injecting 2 bar of ethylene and releasing the ethylene, and repeating this operation 4 times. 1 bar of hydrogen was then injected, and 30 cm<sup>3</sup> of a toluene solution of methylaluminoxane (10.5% by weight of methylaluminoxane, molecular weight 750 g/mol according to cryoscopic determination). The reactor contents were heated to 60°C over the course of 15 minutes with stirring. The overall pressure was then increased to 7 bar by introducing ethylene with stirring at 250 rpm. At the same time, 3.1 mg of metallocene A were dissolved in 20 cm<sup>3</sup> of a toluene solution of methylaluminoxane (concentration and quality as above) and pre-activated by being left to stand for 15 minutes. The solution was then introduced into the reactor. The polymerization system was warmed to a temperature of 65°C and then kept at this temperature for 1 hour by means of suitable cooling. The overall pressure was kept at 7 bar during this time by corresponding supply of ethylene. 160 g of polyethylene were obtained.

The following values were determined on the product:  
VN = 152 cm<sup>3</sup>/g, bulk density: 320 g/dm<sup>3</sup>

**Examples 21-42:**

The procedure was in each case analogous to Example 20, but the following parameters were varied:

- metallocene type

- metallocene quantity (mg)
- methylaluminoxane solution type (content of methylaluminoxane in % by weight, molecular weight M of the methylaluminoxane in g/mol according to cryoscopic determination)
- amount of methylaluminoxane solution (cm<sup>3</sup>) introduced into the reactor
- amount of hydrogen employed (H<sub>2</sub> in bar, no hydrogen was employed in numerous experiments)
- overall pressure P (bar)
- polymerization time t (min)
- polymerization temperature T (°C)

The polymerization parameters which were varied are shown in Table 3, and the polymerization results are shown in Table 4.

**Example 43:**

10 dm<sup>3</sup> of petroleum ether (boiling range 100-120°C) were introduced at 20°C into a dry 16 dm<sup>3</sup> reactor which had been flushed with nitrogen. The gas space of the reactor was then flushed free from nitrogen by injecting 2 bar of ethylene and releasing the ethylene, and repeating this operation 4 times. 200 cm<sup>3</sup> of 1-hexane and 30 cm<sup>3</sup> of a toluene solution of methylaluminoxane (10.6% by weight of methylaluminoxane, molecular weight 900 g/mol according to cryoscopic determination) were then added. The reactor was then heated to 60°C over the course of 15 minutes with stirring. The overall pressure was then increased to 5 bar by introducing ethylene with stirring at 250 rpm. At the same time, 1.3 mg of metallocene E were dissolved in 20 cm<sup>3</sup> of a toluene solution of methylaluminoxane (concentration and quality as above) and preactivated by being left to stand for 15 minutes. The solution was then introduced into the reactor. The polymerization system was warmed to a temperature of 80°C and then kept at this temperature for 45 minutes by suitable cooling. The overall pressure was kept at 5 bar during this time by appropriate supply of ethylene.

380 g of ethylene-1-hexene copolymer were obtained. The following values were determined on the product:

VN = 182 cm<sup>3</sup>/g

density: 0.934 g/cm<sup>3</sup>.

5      **Example 44:**

10 dm<sup>3</sup> of petroleum ether (boiling range 100-120°C) were introduced at 20°C into a dry 16 dm<sup>3</sup> reactor which had been flushed with nitrogen. The gas space of the reactor was then flushed free from nitrogen by injecting 2 bar of ethylene and releasing the ethylene, and repeating this operation 4 times. 400 cm<sup>3</sup> of 1-hexane and 30 cm<sup>3</sup> of a toluene solution of methylaluminoxane (10.6% by weight of methylaluminoxane, molecular weight 900 g/mol according to cryoscopic determination) were then added. The reactor was then heated to 60°C over the course of 15 minutes with stirring. The overall pressure was then increased to 5 bar by introducing ethylene with stirring at 250 rpm. At the same time, 1.3 mg of metallocene B were dissolved in 20 cm<sup>3</sup> of a toluene solution of methylaluminoxane (concentration and quality as above) and preactivated by being left to stand for 15 minutes. The solution was then introduced into the reactor. The polymerization system was warmed to a temperature of 70°C and then kept at this temperature for 45 minutes by suitable cooling. The overall pressure was kept at 5 bar during this time by appropriate supply of ethylene.

520 g of ethylene-1-hexene copolymer were obtained. The following values were determined on the product:

VN = 168 cm<sup>3</sup>/g

30      density: 0.924 g/cm<sup>3</sup>.

**Example 45:**

200 g of sodium chloride were introduced as a stirring aid in the gas phase at 20°C and under atmospheric pressure into a dry 1.5 dm<sup>3</sup> reactor equipped with paddle stirrer which had been flushed with nitrogen. 5 bar of ethylene were then injected, and the stirrer was set at

5 600 rpm. 5 cm<sup>3</sup> of a toluene solution of methylaluminoxane (29.3% by weight of methylaluminoxane having a molecular weight of 1100 g/mol according to cryoscopic determination) were then injected into the reactor by means of a spray nozzle, and the contents were stirred for 15 minutes.

10 At the same time, 1.1 mg of metallocene B were dissolved in 3 cm<sup>3</sup> of a toluene solution of methylaluminoxane (concentration and quality as above) and preactivated by being left to stand for 15 minutes. This solution was then likewise injected into the reactor by means of a spray nozzle, and the temperature of the system was increased to 80°C. After a polymerization time of 20 minutes, the reactor was decompressed, the contents were removed, and the polymer formed was isolated by dissolving the sodium chloride in water, and filtering off and drying the product.

15 14.5 g of polyethylene having VN = 240 cm<sup>3</sup>/g were obtained.

20 **Example 46:**

The procedure was as in Example 45, but the 1.1 mg of metallocene B were replaced by 0.9 mg of metallocene E. 10.4 g of polyethylene having a viscosity number VN = 230 cm<sup>3</sup>/g were obtained.

Table 2

	Metallocene	Abbreviation
	rac-Dimethylsilylbis(1-indenyl)zirconium dichloride	A
5	rac-Diphenylsilylbis(1-indenyl)zirconium dichloride	B
	rac-Phenylmethylsilylbis(1-indenyl)zirconium dichloride	C
10	rac-Phenylvinylsilylbis(1-indenyl)zirconium dichloride	D
	rac-Dimethylgermylbis(1-indenyl)zirconium dichloride	E
15	1-Silacyclobutylbis(1'-indenyl)zirconium dichloride (isomer mixture: 57% of rac-isomer, 43% of meso-isomer)	F
	rac-Dimethylsilylbis(1-(3-methylindenyl))-zirconium dichloride	G
	rac-1,1,2,2-Tetramethyldisilaethylenebis-(1'-indenyl)zirconium dichloride	H
20	rac-1,1,4,4-Tetramethyl-1,4-disilabutylenebis-(1'-indenyl)zirconium dichloride	I
	Dimethylsilylbis(1-(3-trimethylsilyl)cyclopentadienyl)zirconium dichloride (isomer mixture: 43% of rac-isomer, 57% of meso-isomer)	K
25	rac-Ethylenebis(1-indenyl)zirconium dichloride	L
	Propylenebis(1-indenyl)zirconium dichloride	M
	Ethylenebis(1-(3-trimethylsilylindenyl))zirconium dichloride (isomer mixture: 78% of rac-isomer, 22% of meso-isomer)	N
30	rac-Ethylenebis(1-(3-allyldimethylsilylindenyl))-zirconium dichloride	O
	Isopropyl(1-indenyl)cyclopentadienylzirconium dichloride	P
35	Diphenylmethylene(9-fluorenyl)cyclopentadienylzirconium dichloride	Q
	rac-1,1,2,2-Tetramethyldisilaethylenebis(1'-indenyl)hafnium dichloride	R
	Phenylmethylmethylene(9-fluorenyl)cyclopentadienylhafnium dichloride	T



Table 3

Example	Metallocene		MAO solution			H <sub>2</sub>	P	t	T
	Type	Amount (mg)	Content (% by weight)	MM (g/mol)	Amount in reactor (cm <sup>3</sup> )	(bar)	(bar)	(min)	(°C)
5	21	A	4.0	10.5	750	50	-	5	60 65
	22	B	3.9	10.6	900	30	-	5	60 65
	23	C	7.2	10.7	1200	30	-	5	60 65
	24	D	12.2	10.6	900	30	-	5	60 65
10	25	E	8.0	10.6	900	30	-	5	60 65
	26	F	5.9	10.6	900	30	-	5	60 65
	27	G	2.5	10.5	750	30	-	5	60 65
	28	G	1.3	10.5	750	50	-	5	60 65
	29	G	1.2	10.6	900	30	2	5	60 75
15	30	H	1.4	9.9	1100	30	-	5	60 65
	31	I	48.3	9.9	1100	30	-	5	60 65
	32	K	5.3	9.7	1000	60	-	5	60 70
	33	L	1.2	10.1	1300	40	-	5	300 65
	34	M	7.3	9.9	1100	30	-	6	60 65
20	35	M	4.3	10.1	1300	30	-	5	120 65
	36	N	6.8	9.9	1100	30	-	6	65 65
	37	N	3.9	10.1	1300	30	0.5	5.5	80 65
	38	O	11.6	10.7	1200	30	-	5	60 65
	39	P	30.5	10.6	900	30	-	5	60 65
25	40	Q	5.0	10.6	900	30	-	5	60 65
	41	R	6.9	10.1	1300	30	-	5	60 65
	42	T	21.6	10.7	1200	30	-	6	60 65

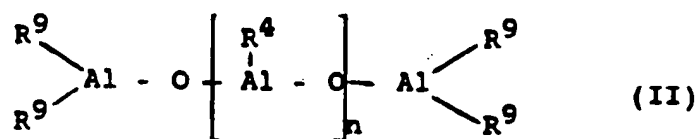
Table 4

	Example	Polymer yield (g)	VN (cm <sup>3</sup> /g)	M <sub>w</sub> (g/mol)	M <sub>w</sub> /M <sub>n</sub>	Bulk density (g/dm <sup>3</sup> )	d <sub>50</sub> (μm)
5	21	300	323	n.m.	n.m.	210	50
	22	140	361	n.m.	n.m.	280	n.m.
	23	65	268	n.m.	n.m.	300	n.m.
	24	90	319	n.m.	n.m.	310	n.m.
	25	290	366	n.m.	n.m.	140	n.m.
10	26	140	392	n.m.	n.m.	180	n.m.
	27	450	323	190000	4.5	170	150
	28	500	313	n.m.	n.m.	200	180
	29	240	36	n.m.	n.m.	400	n.m.
	30	170	911	720000	3.5	210	3500
15	31	590	642	480000	3.7	60	n.m.
	32	1450	162	n.m.	n.m.	300	50
	33	590	198	n.m.	n.m.	140	580
	34	220	551	400000	4.0	70	n.m.
	35	310	624	n.m.	n.m.	80	30
20	36	480	227	120000	2.3	120	n.m.
	37	450	147	n.m.	n.m.	300	n.m.
	38	75	230	n.m.	n.m.	230	n.m.
	39	150	78	n.m.	n.m.	200	n.m.
	40	100	746	n.m.	n.m.	130	n.m.
25	41	35	1222	n.m.	n.m.	n.m.	n.m.
	42	60	711	n.m.	n.m.	n.m.	n.m.

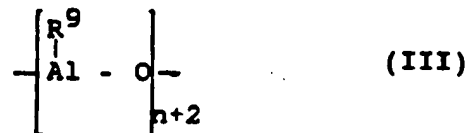
n.m. - not measured

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

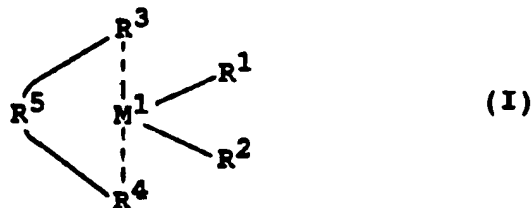
1. A process for the preparation of ethylene polymers by polymerization of ethylene or copolymerization of ethylene with 1-olefins having 3 to 20 carbon atoms at a temperature of from -60 to 200°C and a pressure of from 0.5 to 200 bar in solution, in suspension or in the gas phase, in the presence of a catalyst comprising a metallocene as the transition-metal component and an aluminoxane of the formula II



for the linear type and/or of the formula III



for the cyclic type, where, in the formulae II and III, R<sup>9</sup> is a C<sub>1</sub>-C<sub>8</sub>-alkyl group or phenyl or benzyl, and n is an integer from 2 to 50, which comprises carrying out the polymerization in the presence of a catalyst whose transition-metal component is a compound of the formula I



in which

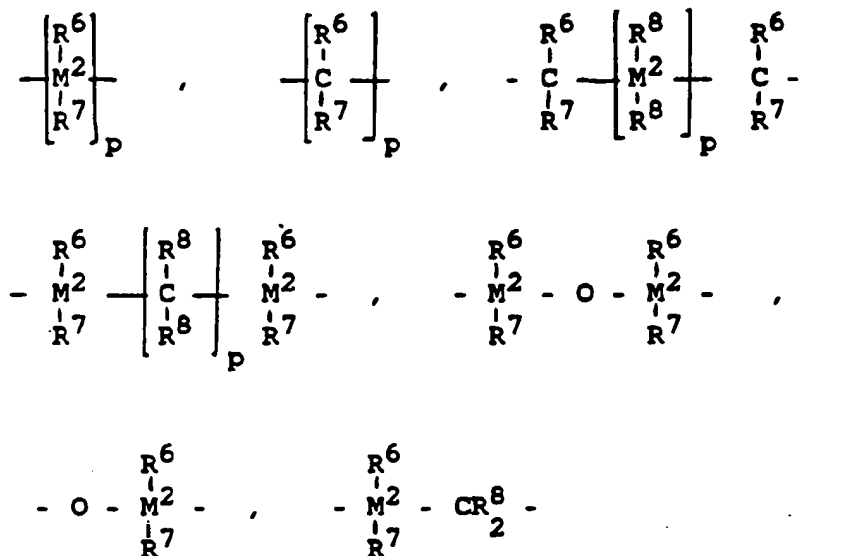
M<sup>1</sup> is titanium, zirconium, hafnium, vanadium, niobium or tantalum,

R<sup>1</sup> and R<sup>2</sup> are identical or different and are a hydrogen atom, a halogen atom, a C<sub>1</sub>-C<sub>10</sub>-alkyl group, a C<sub>1</sub>-C<sub>10</sub>-alkoxy group, a C<sub>6</sub>-C<sub>10</sub>-aryl group, a C<sub>6</sub>-C<sub>10</sub>-aryloxy group, a C<sub>2</sub>-C<sub>10</sub>-alkenyl group, a C<sub>7</sub>-C<sub>40</sub>-arylalkyl group, a C<sub>7</sub>-C<sub>40</sub>-alkylaryl group or

a C<sub>8</sub>-C<sub>40</sub>-arylalk nyl group,

R<sup>3</sup> and R<sup>4</sup> are identical or different and are indenyl, or fluorenyl, having additional substituents, which with the central atom M<sup>1</sup>, is able to form a sandwich structure,

R<sup>5</sup> is



=BR<sup>6</sup>, =AlR<sup>6</sup>, -Ge-, -Sn-, -O-, -S-, =SO, =SO<sub>2</sub>, =NR<sup>6</sup>, =CO, =PR<sup>6</sup> or =P(O)R<sup>6</sup>, where R<sup>6</sup>, R<sup>7</sup> and R<sup>8</sup> are identical or different and are a hydrogen atom, a halogen atom, a C<sub>1</sub>-C<sub>10</sub>-alkyl group, a C<sub>1</sub>-C<sub>10</sub>-fluoroalkyl group, a C<sub>8</sub>-C<sub>10</sub>-fluoroaryl group, a C<sub>8</sub>-C<sub>10</sub>-aryl group, a C<sub>1</sub>-C<sub>10</sub>-alkoxy group, a C<sub>2</sub>-C<sub>10</sub>-alkenyl group, a C<sub>7</sub>-C<sub>40</sub>-arylalkyl group, a C<sub>8</sub>-C<sub>40</sub>-arylalkenyl group or a C<sub>7</sub>-C<sub>40</sub>-alkylaryl group, or R<sup>6</sup> and R<sup>7</sup> or R<sup>6</sup> and R<sup>8</sup>, in each case with the atoms connecting them, form a ring,

M<sup>2</sup> is silicon, germanium or tin, and

p is the number 1, 2, 3, 4 or 5,

or the transition-metal component is

diphenylmethylen (9-fluorenyl) cyclopentadienyl-zirconium dichloride,

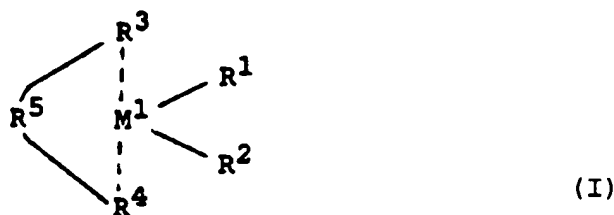
phenylmethylen (9-fluorenyl)

cyclopentadienylhafnium dichloride,

Rac-dimethylsilylbis (1-(3-methylindenyl))

zirconium dichloride.

2. A metallocene of the formula I:



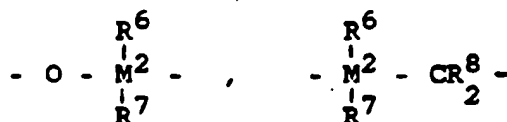
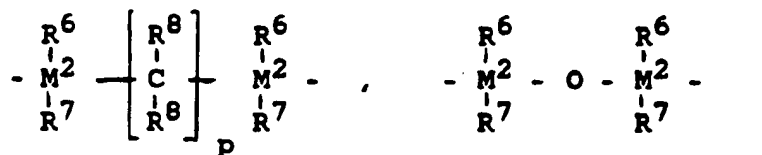
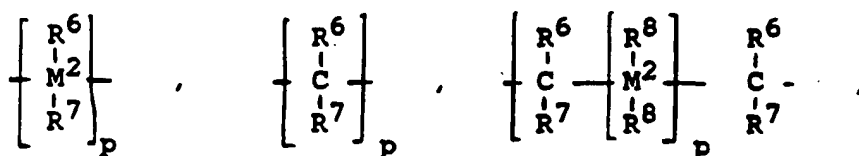
in which

M<sup>1</sup> is titanium, zirconium, hafnium, vanadium, niobium or tantalum,

R<sup>1</sup> and R<sup>2</sup> are identical or different and are a hydrogen atom, a halogen atom, a C<sub>1</sub>-C<sub>10</sub>-alkyl group, a C<sub>1</sub>-C<sub>10</sub>-alkoxy group, a C<sub>6</sub>-C<sub>10</sub>-aryl group, a C<sub>6</sub>-C<sub>10</sub>-aryloxy group, a C<sub>2</sub>-C<sub>10</sub>-alkenyl group, a C<sub>7</sub>-C<sub>40</sub>-arylalkyl group, a C<sub>7</sub>-C<sub>40</sub>-alkylaryl group or a C<sub>8</sub>-C<sub>40</sub>-arylalkenyl group,

R<sup>3</sup> and R<sup>4</sup> are identical or different and are indenyl, or fluorenyl, having additional substituents, which, with the central atom M<sup>1</sup>, is able to form a sandwich structure,

R<sup>5</sup> is



= BR<sup>6</sup>, = AlR<sup>6</sup>, -Ge-, -Sn-, -O-, -S-, = SO, = SO<sub>2</sub>, = NR<sup>6</sup>, = CO, = PR<sup>6</sup> or = P(O)R<sup>6</sup>, where R<sup>6</sup>, R<sup>7</sup> and R<sup>8</sup> are identical or different and are a hydrogen atom, a halogen atom, a C<sub>1</sub>-C<sub>10</sub>-alkyl group, a C<sub>1</sub>-C<sub>10</sub>-fluoroalkyl group, a C<sub>6</sub>-C<sub>10</sub>-fluoroaryl group, a C<sub>6</sub>-C<sub>10</sub>-aryl group, a C<sub>1</sub>-C<sub>10</sub>-alkoxy group, a C<sub>2</sub>-C<sub>10</sub>-alkenyl group, a C<sub>7</sub>-C<sub>40</sub>-arylalkyl group, a C<sub>8</sub>-C<sub>40</sub>-arylalkenyl group, or a C<sub>7</sub>-C<sub>40</sub>-alkylaryl group, or R<sup>6</sup> and R<sup>7</sup> or R<sup>6</sup> and R<sup>8</sup>, in each case with the atoms connecting them, form a ring,

M<sup>2</sup> is silicon, germanium or tin, and

p is the number 1, 2, 3, 4 or 5.

3. The metallocene as claimed in claim 2 wherein:

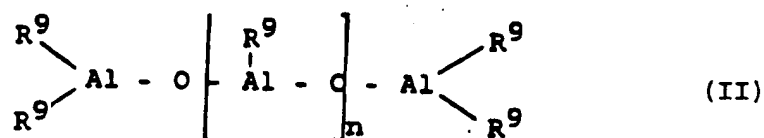
M<sup>1</sup> is zirconium;

R<sup>1</sup> and R<sup>2</sup> are a hydrogen atom, C<sub>1</sub>-C<sub>3</sub>-alkyl, C<sub>1</sub>-C<sub>3</sub>-alkoxy, C<sub>6</sub>-C<sub>8</sub>-aryl, C<sub>6</sub>-C<sub>8</sub>-aryloxy, C<sub>2</sub>-C<sub>4</sub>-alkenyl, C<sub>7</sub>-C<sub>10</sub>-arylalkyl; C<sub>7</sub>-C<sub>12</sub>-alkylaryl, C<sub>8</sub>-C<sub>12</sub>-arylalkenyl or chlorine;

M<sup>2</sup> is silicon or germanium; and

p is the number 1, 2, 3, 4 or 5.

4. A metallocene as claimed in claim 2 which is  
diphenylmethylene (9-fluorenyl)  
cyclopentadienylzirconium dichloride,  
phenylmethoxymethylene (9-fluorenyl)  
cyclopentadienylhafnium dichloride, rac-  
dimethylsilylbis (1-(3-methylindenyl))-zirconium  
dichloride.
  
5. A catalyst comprising:
  - (a) a metallocene as claimed in any one of claims  
2-4; and
  - (b) an aluminoxane.
  
6. The catalyst according to claim 5 wherein the  
aluminoxane is of the formula II



or



wherein:

R<sup>9</sup> is a C<sub>1</sub>-C<sub>6</sub> alkyl group or phenyl and n is an  
integer from 2 to 50.